CD221. LECTURE 14. PARTICLE DISTRIBUTION FUNCTION.

• The Probability Distribution of the Energy for a System at Constant T

We've previously shown that for a system at constant T, the probability that it can be found in a *macrostate* with energy U is

$$p_U \equiv p(U) = \frac{1}{Q}\Omega(U,V,N)e^{-\beta U} \tag{1}$$

We also know that at constant V and N, Ω is an increasing function of U (there are more microstates a system can access if it has more energy), whereas $e^{-\beta U}$ is a decreasing function of U. So the product of Ω and $e^{-\beta U}$ is a function that exhibits a rise and a fall; in other words, it has a maximum, U^*. And because the rise and fall are very steep (for macroscopic systems, anyway), the maximum will be sharp and narrow, and we can take it to coincide with the mean itself. To a very good approximation then $U^* = \overline{U}$.

One way we can now get a definite *functional* form for $p(U)$ is to approximate it by a Taylor expansion around U^*. To second order, this expansion is

$$p(U) \approx p(U)|_{U=U^*=\overline{U}} + \frac{1}{2}\frac{\partial^2 p}{\partial U^2}\bigg|_{U=U^*=\overline{U}}(U-U^*)^2 + \cdots \tag{2}$$

There is no first order term in this expansion because by the requirement for a maximum

$$\frac{\partial p}{\partial U}\bigg|_{U=U^*} = 0, \tag{3}$$

Equation (3) determines (implicitly) the value of U^*, which we now find by differentiating $p(U)$ with respect to U:

$$\frac{\partial p}{\partial U} = \frac{1}{Q}\left[e^{-\beta U}\frac{\partial \Omega}{\partial U} - \beta\Omega e^{-\beta U}\right]$$

$$= \frac{\Omega e^{-\beta U}}{Q}\left[\frac{1}{\Omega}\frac{\partial \Omega}{\partial U} - \beta\right]$$

$$= p(U)\left[\frac{\partial \ln \Omega}{\partial U} - \beta\right] \tag{4}$$

For this derivative to be 0 at $U = U^* = \overline{U}$, we require that

$$\frac{\partial \ln \Omega(\overline{U})}{\partial \overline{U}} = \beta \tag{5}$$

We can use this condition to simplify the second derivative term in Eq. (2), following these steps:

$$\frac{\partial^2 p}{\partial U^2} = \frac{\partial}{\partial U} \frac{\partial p}{\partial U} = \frac{\partial}{\partial U} p(U) \left[\frac{\partial \ln \Omega}{\partial U} - \beta \right] \quad \text{(using the last line of Eq. (4))}$$

$$= \frac{\partial p(U)}{\partial U} \left(\frac{\partial \ln \Omega}{\partial U} - \beta \right) + p(U) \frac{\partial^2 \ln \Omega}{\partial U^2} \tag{6}$$

At $U = U^* = \overline{U}$, Eq. (6) reduces to

$$\left. \frac{\partial^2 p}{\partial U^2} \right|_{U = \overline{U}} = p(\overline{U}) \frac{\partial^2 \ln \Omega(\overline{U})}{\partial \overline{U}^2}$$

$$= p(\overline{U}) \frac{\partial}{\partial \overline{U}} \frac{\partial \ln \Omega(\overline{U})}{\partial \overline{U}}$$

$$= p(\overline{U}) \frac{\partial \beta}{\partial \overline{U}} \quad \text{(using Eq. (5))}$$

$$= p(\overline{U}) \left(\frac{\partial \overline{U}}{\partial \beta} \right)^{-1} = -p(\overline{U}) \frac{1}{k_B T^2 C_V} \tag{7}$$

where in order to get the second equality we've used the definition $C_V = (\partial U / \partial T)_{V,N}$. If Eq. (7) is now substituted into Eq. (2), we get

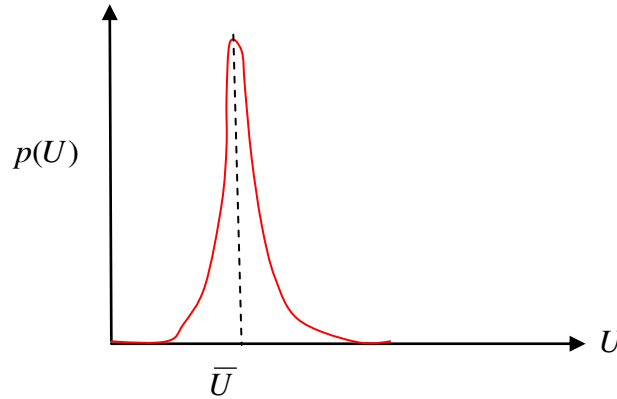$$p(U) \approx p(\overline{U}) - \frac{1}{2 k_B T^2 C_V} p(\overline{U})(U - U^*)^2 + \cdots$$

which can be approximated as

$$p(U) \approx p(\overline{U}) \left[\exp\left(-\frac{1}{2 k_B T^2 C_V} (U - \overline{U})^2 \right) \right] \tag{8}$$

Furthermore, because probabilities must be normalized, we can apply the formula $\int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\pi/a}$ to Eq. (8) and show that $p(\overline{U}) = 1/\sqrt{2\pi k_B T^2 C_V}$. The complete expression for $p(U)$ is therefore

$$p(U) \approx \frac{1}{\sqrt{2\pi k_B T^2 C_V}}\left[\exp\left(-\frac{1}{2k_B T^2 C_V}(U-\overline{U})^2\right)\right] \tag{9}$$

and we see that it is a Gaussian, which looks roughly like this:

Knowing $p(U)$, we're now in a position to answer questions like this: what is the probability that 1 mole of an ideal gas under standard conditions will be observed, say, with an energy $U = 0.1\overline{U}$?

• Fluctuations in Systems With Different Constraints: The Case of Fixed *T, V* and μ

The statistical properties of fluctuations in other kinds of systems can be similarly derived. Consider, for instance, a system at fixed *T, V* and μ. In such a system, both the energy and number of particles fluctuate, and as an illustrative exercise let's calculate the variance in *N*, viz.,

$$\sigma_N^2 = \overline{N^2} - \overline{N}^2 = \sum_{\alpha} p_{\alpha} N_{\alpha}^2 - \left(\sum_{\alpha} p_{\alpha} N_{\alpha}\right)^2 \tag{10}$$

For systems at constant *T* and , we've shown that p_{α} is given by

$$p_{\alpha} = \frac{1}{\Xi} e^{-\beta(U_{\alpha} - \mu N_{\alpha})} \tag{11}$$

Therefore,

$$\sum_\alpha p_\alpha N_\alpha^2 = \frac{1}{\Xi} \sum_\alpha N_\alpha^2 e^{-\beta(U_\alpha - \mu N_\alpha)}$$

$$= \frac{1}{\Xi \beta^2} \frac{\partial^2}{\partial \mu^2} \sum_\alpha e^{-\beta(U_\alpha - \mu N_\alpha)}$$

$$= \frac{1}{\Xi \beta^2} \frac{\partial^2 \Xi}{\partial \mu^2} \tag{12}$$

In the same way,

$$\sum_\alpha p_\alpha N_\alpha = \frac{1}{\Xi} \sum_\alpha N_\alpha e^{-\beta(U_\alpha - \mu N_\alpha)}$$

$$= \frac{1}{\Xi \beta} \frac{\partial}{\partial \mu} \sum_\alpha e^{-\beta(U_\alpha - \mu N_\alpha)}$$

$$= \frac{1}{\Xi \beta} \frac{\partial \Xi}{\partial \mu} \tag{13}$$

Substituting Eqs. (12) and (13) into Eq. (10), we arrive at

$$\sigma_N^2 = \frac{1}{\beta^2} \left[\frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial \mu^2} - \frac{1}{\Xi^2} \left(\frac{\partial \Xi}{\partial \mu} \right)^2 \right]$$

$$= \frac{1}{\beta^2} \frac{\partial^2 \ln \Xi}{\partial \mu^2}$$

$$= \frac{1}{\beta^2} \frac{\partial^2 \ln \Xi}{\partial \mu^2}$$

$$= -\frac{1}{\beta^2} \frac{\partial^2 \beta \Psi}{\partial \mu^2} \tag{14}$$

where Ψ is the grand potential, and the derivatives in Eq. (14) are taken at constant values of T and V. To simplify Eq. (14), we recall the differential form of the grand potential,

$$d\Psi = -SdT - PdV - \overline{N}d\mu \tag{15}$$

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noting that the coefficient of $d\mu$ is the *average* number of particles $\overline{N}$ and not some arbitrary number of particles N. From Eq. (15) it follows that

$$\left(\frac{\partial \Psi}{\partial \mu}\right)_{T,V} = -\overline{N} \tag{16}$$

and that

$$\left(\frac{\partial^2 \Psi}{\partial \mu^2}\right)_{T,V} = -\left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V} \tag{17}$$

The right hand side of Eq. (17) can be reduced to a more recognizable form by bringing μ to the numerator and eliminating it using the Gibbs-Duhem relation. That is,

$$\left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V} = \left(\frac{\partial \mu}{\partial \overline{N}}\right)_{T,V}^{-1}$$

$$= \left(v\left(\frac{\partial P}{\partial \overline{N}}\right)_{T,V}\right)^{-1} \tag{18}$$

A Maxwell relation can now be used to write the above partial derivative as

$$\left(\frac{\partial P}{\partial \overline{N}}\right)_{T,V} = -\left(\frac{\partial \mu}{\partial V}\right)_{T,\overline{N}} \tag{19}$$

which by further appeal to the Gibbs-Duhem equation leads to

$$\left(\frac{\partial P}{\partial \overline{N}}\right)_{T,V} = -v\left(\frac{\partial P}{\partial V}\right)_{T,\overline{N}} \tag{20}$$

Combining Eqs. (18) and (20), and substituting into Eq. (17), we finally find that

$$\left(\frac{\partial^2 \Psi}{\partial \mu^2}\right)_{T,V} = \frac{\overline{N}^2}{V^2}\left(\frac{\partial V}{\partial P}\right)_{T,\overline{N}} \tag{21}$$

Now recognizing that $V^{-1}(\partial V/\partial P)_{T,\overline{N}} = -\kappa_T$, with κ_T being the isothermal compressibility, we can write the variance of $\overline{N}$ from Eqs. (14) and (21) as

$$\sigma_N^2 = \frac{\overline{N}^2 k_B T \kappa_T}{V} \tag{22}$$

As before it's possible to get an idea of the relative size of the fluctuations by considering the ratio $\sigma_N / \overline{N}$. For an ideal gas, since $\kappa_T = 1/P$, it's easy to see that

$$\frac{\sigma_N}{\overline{N}} = \frac{1}{\overline{N}^{1/2}} \tag{23}$$

and again one sees that the relative size of the particle number fluctuations is very, very small.

• The Probability Distribution of the Particle Number for an Ideal Gas

From our discussion of the energy fluctuations in a system at constant T (at fixed V and N), we've seen that it's only the probability distribution of U, viz., $p(U)$, and not its mean and variance, that can provide complete information about the range and spread of possible U values. The same is true of fluctuations of N in a system at constant T and μ (at fixed V.) So let's now attempt to find the probability distribution, $p(N)$, of N . But rather than derive a general expression for $p(N)$ (applicable to any system), we'll keep things relatively simple by considering the case of – yes, you guessed it, the ideal gas.

We've already derived all of the results we need to calculate $p(N)$ for this system. In particular, we've shown, that

$$p(N) \equiv p_N = \frac{1}{\Xi} Q(T,V,N) e^{\beta \mu N} \tag{24}$$

For the ideal gas, the canonical partition function $Q(T,V,N)$ is given by

$$Q(T,V,N) = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} V^N \tag{25}$$

so in terms of the variable $\xi \equiv (2\pi m k_B T / h^2)^{3/2} V e^{\beta \mu}$, $p(N)$ can be written as

$$p(N) = \frac{\xi^N}{\Xi N!} \tag{26}$$

The two other results we'd derived earlier are the following:

$$\Xi = e^{\xi} \tag{27}$$

and

$$\xi = \overline{N} \qquad (28)$$

and substituting these results into Eq.(26), we finally arrive at

$$p(N) = \frac{\overline{N}^N e^{-\overline{N}}}{N!} \qquad (29)$$

which is the expression we were after. Notice how different in structure $p(N)$ is from $p(U)$. Distributions with the structure of Eq. (29) are called <u>Poisson distributions</u>. They are characterized by a single parameter $\overline{N}$, and if we plot the function for different $\overline{N}$, we get histograms like the following (with μ in the figures standing for $\overline{N}$, not chemical potential):
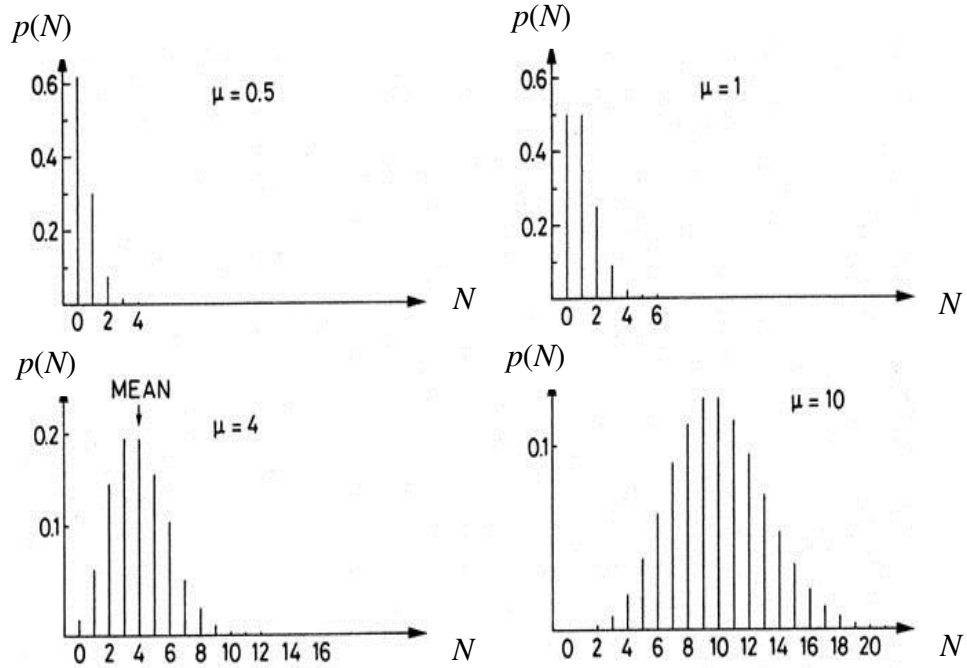
The graphs are histograms because N is discrete, but as N becomes larger and larger, the distribution becomes effectively continuous, and it more nearly resembles a Gaussian.